

Photocatalytic Coatings for Exploration and Spaceport Design

2006 Center Director's Discretionary Fund Project



Corrosion
Control

This project developed self-cleaning photocatalytic coatings that remove contamination without human intervention. The coatings chemically remove organic contaminants and leave no residue. The photocatalyst will not negatively affect other coating properties, especially corrosion resistance.

Titanium dioxide, TiO_2 , is an extremely popular photocatalyst because of its chemical stability, nontoxicity, and low cost. TiO_2 is commonly used in the photocatalytic oxidation of organic matter or pollutants in the gas and liquid phases. However, TiO_2 does have some drawbacks. It has limited light absorption because of its large band-gap and suffers from a photonic efficiency of less than 10 percent for organic degradation. Dopants can lower the band-gap and improve efficiency. Since the photocatalytically active form of TiO_2 is a nanocrystalline powder, it can be difficult to make a robust coating with enough catalyst loading to be effective.

Photocatalysts become active when certain light energy is absorbed. When photons with an energy greater than the band-gap, E_g (wavelengths shorter than 400 nm) impinge upon the surface of the TiO_2 , an electron-hole pair is formed (Figure 1). The electron-hole pair oxidizes adsorbed substances either directly or via reactive intermediates that form on the surface, such as hydroxyl radicals ($\text{OH}\cdot$) or superoxide ions (O_2^-).

Several factors can influence the band-gap energy of TiO_2 , two of which are crystal structure and impurities. TiO_2 exists as three crystal structures—brookite, anatase, and rutile—that can be controlled via heat treatment. Anatase is the most photocatalytically active crystal form of TiO_2 . Doping TiO_2 with impurities can alter its band-gap energy, as well as its effectiveness as a catalyst. Depending on their size, dopant atoms can occupy either the substitutional or interstitial lattice positions. Atoms that are relatively large will assume the interstitial positions and create a much greater energy disturbance in the crystal than will smaller atoms that take on the substitutional positions. This energy disturbance narrows the band-gap and thus allows photons with longer wavelengths and smaller energies (such as those in the visible-light spectrum) to create electron-hole pairs.

Raman spectroscopy was performed for the purpose of determining the crystal structure and the degree of crystallinity of the TiO_2 particles. Reflectance measurements indicated the wavelengths of light absorbed by the different catalysts. Reflectance is inversely proportional to absorbance and can help approximate the band-gap. The wavelength where the percentage of reflectance begins to decrease approximates the band-gap. For pure TiO_2 , only the sample heated to 600 °C exhibits different spectral behavior from the others. Its rutile crystal structure ended its absorbance near a wavelength of 460 nm instead of the 435-nm wavelength characteristic of the other samples in the anatase phase.

For the catalysis evaluation, 20 μL of 0.2-mg/mL Rhodamine B dye in ethanol was added to 10-mg samples of the catalyst. Half of the prepared samples were exposed to ultraviolet (UV) radiation (from an F8T5/BLB fluorescent light with peak emission at 365 nm) for 24 hours, while the other half were kept in the dark. Upon completion of the UV test, the addition of 5 mL of water dissolved the remaining dye. The absorbance of the dye, measured with an HP spectrophotometer, between 450 nm and 615 nm, revealed the amount of dye remaining after exposure. The effectiveness of each catalyst was determined by the comparison of the amount of absorbance of the dye remaining in the samples with the initial absorbance of the dye alone. All measurements were made in triplicate. Figure 2 shows results for the cleaning efficiency of pure TiO_2 made with three different procedures and different heat treatments. Procedure 3 with a heat treatment at 400 °C performed the best. In general for all the doped catalysts, Procedure 3 with the same heat treatment performed the best.

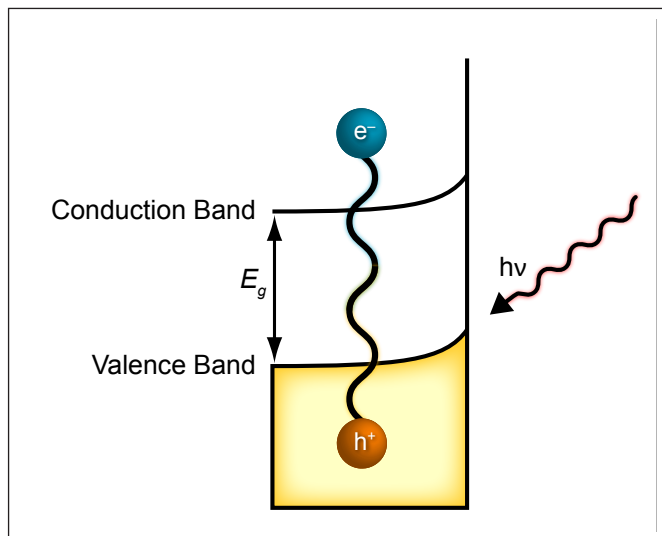


Figure 1. Electronic band structure of a semiconductor showing the electron-hole pair formed after it absorbs a photon of light.

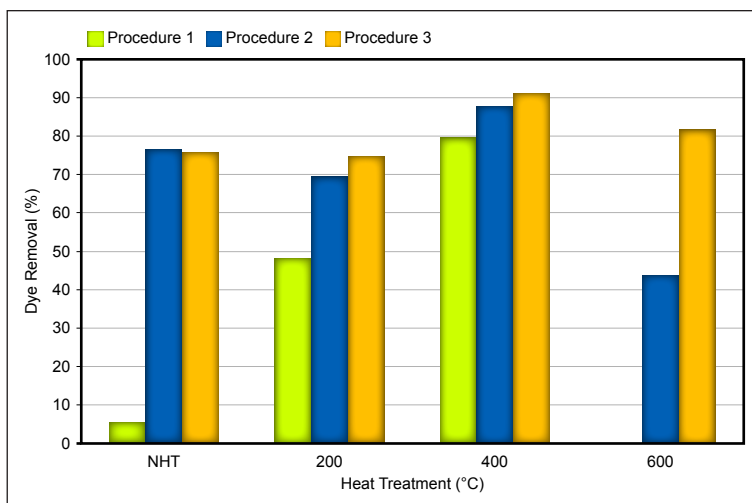


Figure 2. Dye reduction after the catalyst was exposed to UV light for 24 hours. The catalyst was pure TiO_2 made in three ways with different heat treatments. The high percentage reduction indicates that the catalyst oxidized nearly all the dye in contact with the surface. NHT indicates no heat treatment.